THE EXTRACTION CHARACTERISTICS OF THE ETHYLAMINES

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1952

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
August, 1953

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PREFACE

The author wishes to express his gratitude to the Faculty and Staff of the Chemical Engineering Department for their aid and comments during the course of the work presented here.

A special word of appreciation is due Dr. Charles L. Nickolls who served as adviser to the author during the past year and who acted as counselor for this project.

This person is at present a member of the United States Air Force and is indebted to the Air Force Institute of Technology under whose auspices this graduate work was done at Oklahoma A. and M. College.

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INTRODUCTION

Liquid-liquid extraction is the term applied to the Chemical Engineering unit operation in which a material dissolved in a liquid phase is transferred to a second immiscible or nearly immiscible liquid phase by the mechanism of mass transfer.

Interest in the field of liquid-liquid extraction has been increasingly evident in the last few years. A comparatively new addition to the more established unit operations, liquid-liquid extraction occasionally has been found advantageous over the other separation processes available to the engineer, particularly where a separation as to type of molecule is desired rather than to "size" as would be accomplished by distillation.

The theoretical analytics for extraction have been obtained by the extension of theory from other fields such as distillation and absorption. The mechanism of extraction is usually interpreted by the two film theory of diffusion. This theory may or may not be correct but it has been useful as a practical guide to the engineer.

At present, design work for liquid-liquid extraction is generally done by the extension of pilot plant data and a general method of prediction of the various transfer coefficients for a particular system in any given piece of equipment from its physical and chemical properties is still lacking.

Treybal, [15] and Sherwood and Pigford[13] have given comprehensive surveys of the various developments and trends relating to the theory and methods of correlation of liquid-liquid extraction data.

There are three possible methods of interpreting experimental data to express the effectiveness of mass transfer between two liquid phases. They are the over-all coefficient of mass transfer, Ka, the height of a transfer unit, H. T. U., and the height equivalent to a theoretical plate, H.E.T.P.

All of these quantities have been experimentally investigated but the most recent trend favors the H.T.U. method developed by Colburn.[3,4] The individual resistances of each film may be determined by this method by plotting suitable experimental data if certain restrictions are imposed on the system. These film resistances have been used in the past to evaluate the effect of certain variables present in extraction work.[5,9,10,11]

Row, Koffolt, and Withrow[11] used the Colburn H.T.U. method to evaluate their data obtained in a packed column study. They used the variation of the film value of the dispersed phase to relate performance to such variables as packings and flow rates.

Colburn and Welsh[5] used a unique two component system to determine the individual film values for the water-isobutanol system. They showed these film values as functions of the flow rates of the two streams.

Ladda and Smith,[9] using other two component systems, determined the individual film values and found that they could be expressed as a power function of the ratio of the flow rates.

Morello and Beckman[10] investigated the effect of temperature on the extraction of diethylamine from water with toluene by employing the film values of the dispersed phase at four temperatures. The H.T.U. for the water film was found to be essentially zero while the toluene film value varied with temperature.

In the present work, three organic bases, ethylamine, diethylamine, and triethylamine were extracted from water by a dispersed toluene phase in a column packed with small beads. All operating conditions were similar for the three extractions, and it was expected that the individual film values of the two liquid phases would perhaps show some relationship to the physical properties of the diffusing solute being transferred.

These particular solutes were chosen because they are basically similar type compounds and yet have over a two-fold variation in molecular weight, extremely wide variation in their distribution properties, and some variation in their diffusivity values.

The equipment used in these determinations is advantageous for investigating fundamental properties of extraction systems because it provides the best control over the interfacial area in the column.

EXPERIMENTAL STUDY

Analytical Method

The concentrations of the amines used in these experiments were determined by direct titration with hydrochloric acid.

The hydrochloric acid was standardized against C.P. sodium oxalate and sodium bicarbonate by procedures given by Kolthoff and Sandell.[8]

The indicator used was brom-cresol green. The indicator was found to be at its transition color with the distilled water used so it was not necessary to use freshly boiled water.

By adding analytically weighed samples of the three amines to pure toluene, it was determined that accurate determinations could be made of the toluene samples by titration using a large excess of water to extract the amine. This obviated the use of alcohol to make the solutions miscible.

All representative samples analyzed were 5 ml.

Materials Used

The liquids used in these determinations were laboratory distilled water and technical-grade, 95 mole % toluene. The solute grades, form and sources are shown below.

Ethylamine	Fischer Scientific Co.	33% solution-C.P.
Diethylamine	Paragon Laboratories	70% solution
Triethylamine	Matheson Chemical Co.	100% solution-Pract.

Equilibrium Distribution Data

To assure that calculable results could be obtained, it was necessary to determine the equilibrium distribution of the three solutes between water and toluene at 25° C.

Increasing amounts of the three amines were added to mixtures of toluene and water. These mixtures were mechanically shaken for six to eight hours while in an electronically controlled water bath held at 25 ± 0.1° C.

When equilibrium was attained, samples of each phase were withdrawn and titrated with the standardized hydrochloric acid to determine the solute content.

The distribution curves determined from the results of these determinations expressed in moles of solute per liter of solution are shown in Figures 1, 2, and 3. The experimental values are tabulated in Tables 1, 2, and 3.

To calculate the $(H.T.U.)_{ot}$ for triethylamine the equilibrium distribution at comparatively high water concentrations was required. These data were secured from Seidell[12] and may be found in Figure 4 and on Table 4.

Determination of Diffusivity Values

The diffusivity values used to express a portion of the results of this work, were calculated by the empirical method of Wilke.[16] The solvent factor, F, required by this method for the diffusivities in toluene was determined for toluene from the value for the diffusion of iodine in toluene obtained from the International Critical Tables.[7]

The diffusivities of the solutes at 25° C. in water and in toluene

Table 1

Equilibrium Distribution of Ethylamine between Water and Toluene at 25 ± 0.1° C.

Concentrations, gm.-moles/liter

Toluene Phase	Water Phase
0.00405	0.0725
0.00445	0.0691
0.01011	0.1797
0.01106	0.1932
0.0159	0.271
0.0205	0.350
0.0213	0.362
0.0244	0.410

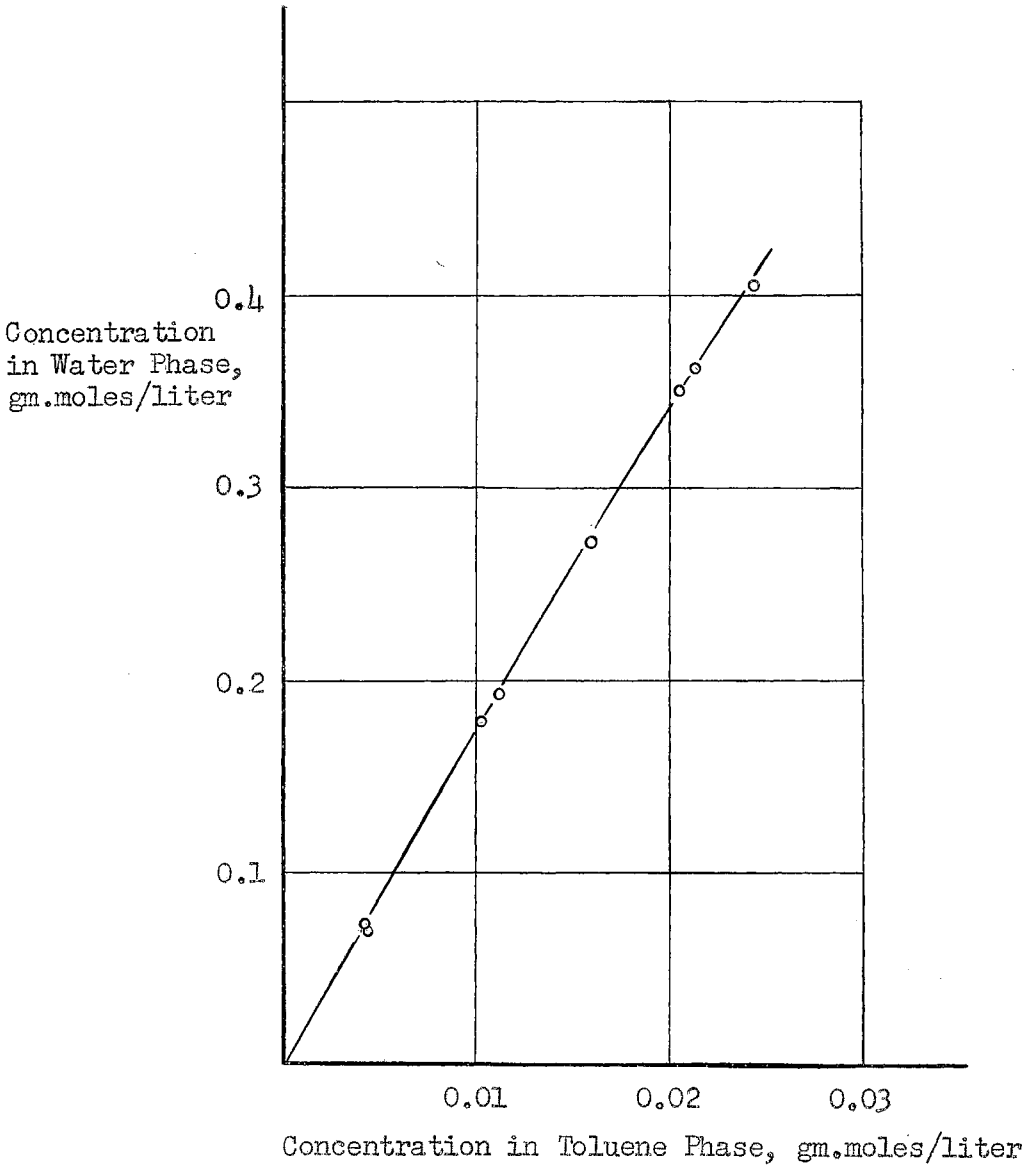


Figure 1

Equilibrium Distribution of Ethylamine Between

Water and Toluene at 25 $\pm$ 0.1° C.

Table 2

Equilibrium Distribution of Diethylamine between Water and Toluene at 25 ± 0.1° C.

Concentrations, gm.-moles/liter	
Toluene Phase	Water Phase
0.01011	0.01619
0.01646	0.02720
0.0426	0.0664
0.0523	0.0795
0.0532	0.0810
0.0580	0.0880
0.0618	0.0920

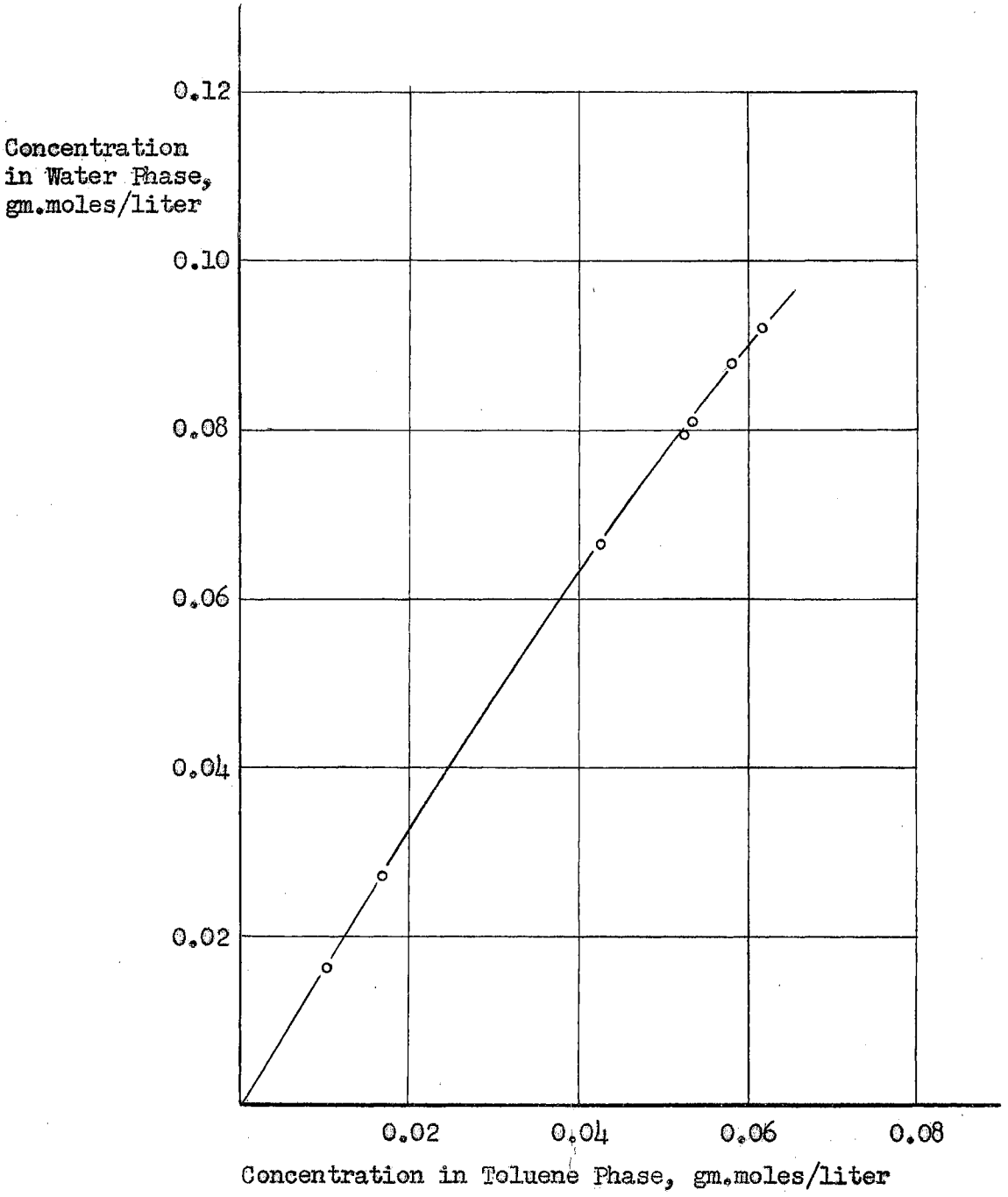


Figure 2

Equilibrium Distribution of Diethylamine Between Water and Toluene at 25 ± 0.1° C.

Table 3

Equilibrium Distribution of Triethylamine between Toluene and Water at 25 ± 0.1° C. (Low Water Concentration)

Concentrations, gm.-moles/liter

Toluene Phase	Water Phase
0.0109	0.00216
0.0286	0.00418
0.0431	0.00566
0.0605	0.00755
0.1402	0.0148
0.1502	0.0155
0.1931	0.01995
0.251	0.0251

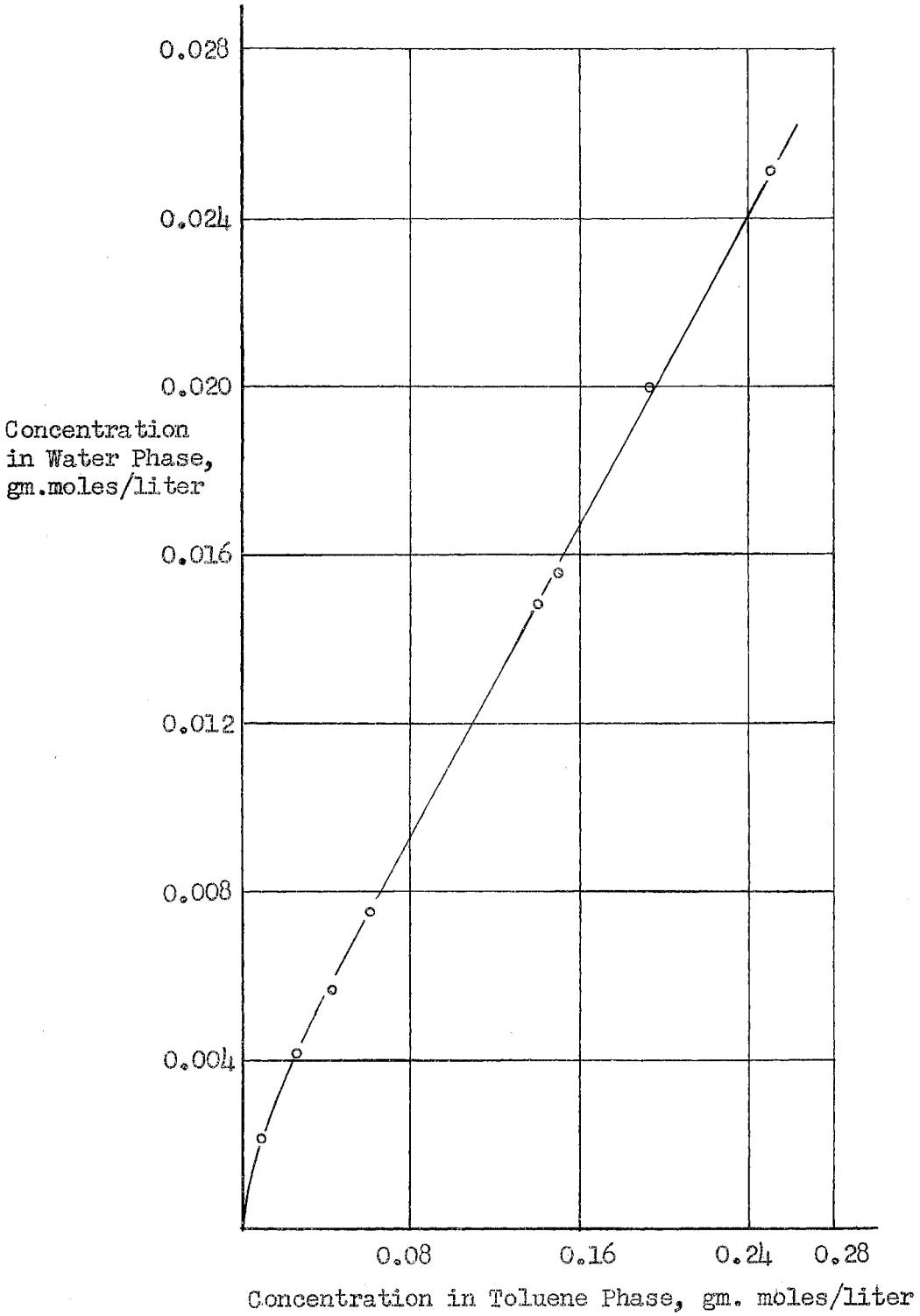


Figure 3

Equilibrium Distribution of Triethylamine Between Water and Toluene at 25 ± 0.1° C.

(Low Water Phase Content)

Table 4

Equilibrium Distribution of Triethylamine between Toluene and Water at 25° C.
(High Water Concentration, Seidell[12])

Concentrations, gm.-moles/liter

Toluene Phase	Water Phase
0.0239	0.0046
0.0579	0.0069
0.0792	0.0096
1.0804	0.1042
1.7390	0.1518
4.5160	0.2941
5.5340	0.3577

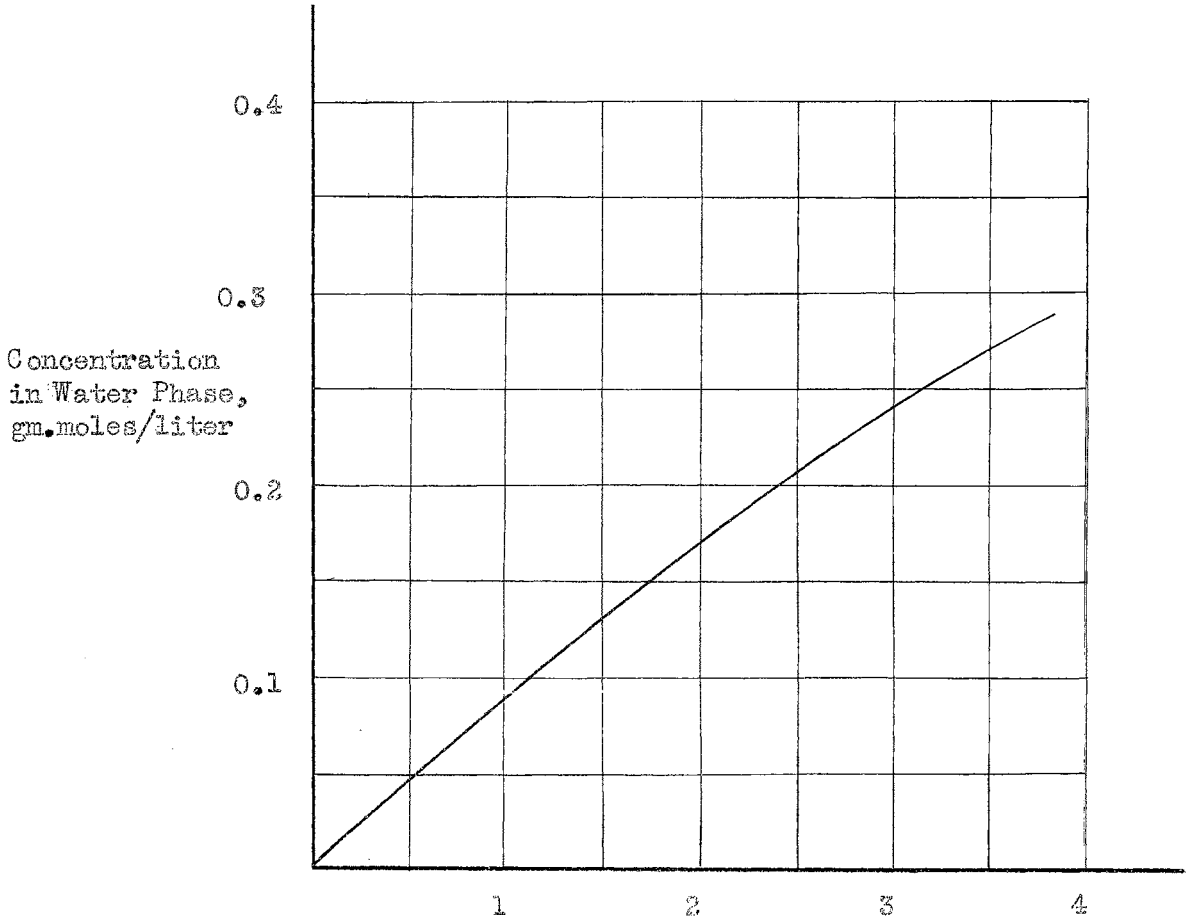


Figure 4

Equilibrium Distribution of Triethylamine

Between Water and Toluene at 25° C.

(High Water Phase Content)

Table 5

Diffusivities, Molecular Weights, and Molal Volumes of Ethylamine, Diethylamine, and Triethylamine

	Diffusivity in Water (sq. cm. per sec.)	Diffusivity in Toluene (sq. cm. per sec.)
Ethylamine	1.13×10^{-5}	2.11×10^{-5}
Diethylamine	0.811	1.52
Triethylamine	0.646	1.23

	Molecular Weight	Molal Volume
Ethylamine	66.0	45.08
Diethylamine	111.9	73.14
Triethylamine	159.9	101.19

are shown in Table 5. Included in this table are the molal volumes and molecular weights of the three amines.

Countercurrent Extraction-Equipment

The extraction column used for these determinations was a heavy-duty Pyrex tube 62 in. long and 1.5 in. inside diameter. It was packed to a height of 4.5 feet with 4-mm. glass beads except in Run II-1 and II-2 when the packed height was 3 feet. The small glass beads of the packing were supported by a few small berl saddles which rested on a perforated glass disk which served as the packing support. The continuous water phase was introduced into the column just below the top of the packing, and the dispersed toluene phase entered just above the packing support.

All liquid lines were either glass or tygon tubing. The exit lines for both the continuous and dispersed phase were vented, and the continuous phase discharge line was adjustable to provide a control for adjusting the height of the interface.

The water and toluene feed solutions were moved through the column by compressed air maintained at a pressure of 9 psig. in the feed storage bottles.

The flow rate of the feed solutions was indicated by the pressure drop across a constriction in each feed line. These pressure drops were indicated on mercury-filled inclined-tube manometers. The manometer readings were used as an indication of continuity only. The flow rates for each run were determined volumetrically by collecting the solutions leaving the column.

Storage vessels for the feed and product solutions were 5 and 12 gallon Pyrex carboys respectively.

The temperature control system for the extraction equipment consisted of a 15-gallon water tank equipped with an electric heating coil capable of maintaining the temperature in the tank at 25 ± 1° C. The water from this tank flowed by gravity into two large containers in which the 5-gallon feed carboys rested. The control water was pumped from these containers through a 3-in. outside diameter Pyrex tube which enclosed the packed section of the column and then drained back into the control tank.

A thermometer well at the top of the column near the discharge point for the toluene phase was used as a check point for the temperature of the liquid in the column.

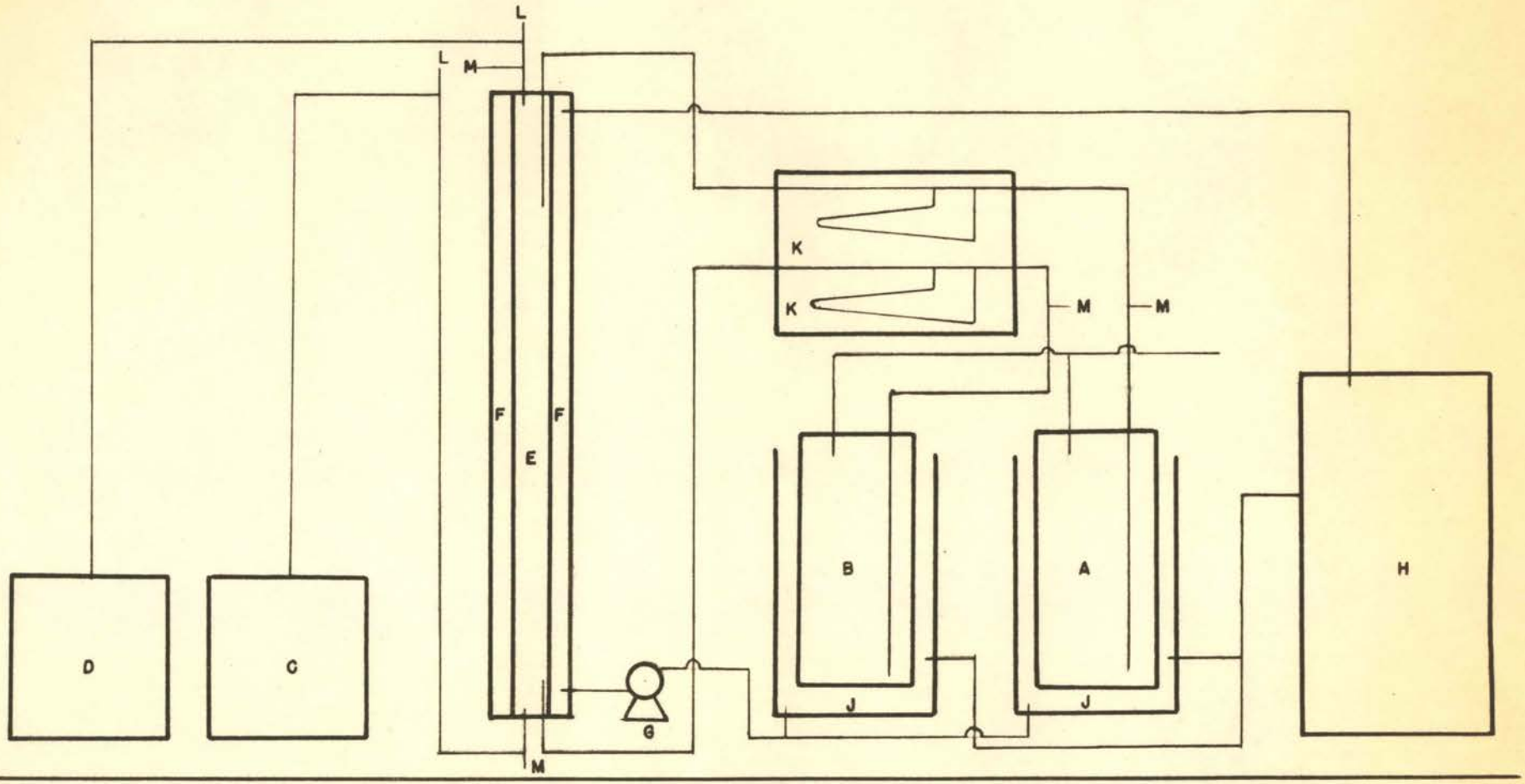
A schematic drawing of the equipment is presented in Figure 5, and a photograph of the equipment and its auxiliaries is shown in Figure 6.

Countercurrent Extraction-Operational Procedure

The continuous countercurrent extraction data were determined in the following way.

The amine-water feed solution was adjusted to approximately the concentration of the previous run and placed in the carboy in the constant temperature water tank.

The toluene product from the previous run was washed three times with dilute sulfuric acid and then washed in a 12-gallon carboy for five to six hours by a finely dispersed spray of water introduced through a stainless steel tube containing 40 small holes. It was washed until there was no trace of amine remaining. The toluene was then put in a 5-gallon



A = WATER FEED STORAGE
B = TOLUENE FEED STORAGE
C = WATER PRODUCT
D = TOLUENE PRODUCT
E = PACKED COLUMN
F = WATER JACKET
G = CONTROL WATER PUMP
H = CONSTANT TEMP. TANK
J = FEED WATER BATH
K = FLOW RATE MANOMETERS
L = OUTLET VENTS
M = SAMPLE POINTS

SCHEMATIC FLOW DIAGRAM OF EQUIPMENT USED

FIGURE 5

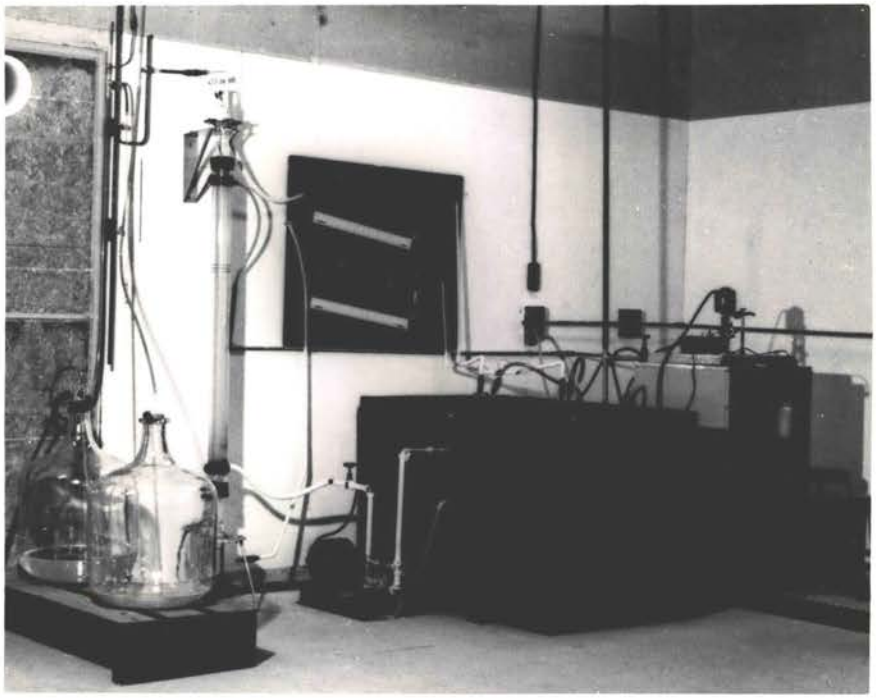


Figure 6

Photograph of the Liquid-Liquid Extraction

Countercurrent Equipment

carboy and placed in its constant temperature tank.

When the feed solutions reached the temperature of the control bath, the compressed air was adjusted to 9 psig. and the needle valve controlling the flow of the continuous water phase was opened and adjusted until the inclined tube manometer gave the desired reading for the particular run.

When the column was about one-fourth filled, the dispersed phase was introduced and its flow rate adjusted roughly to the desired value by the manometer reading.

After the interface appeared above the top of the packing, the height of the water phase discharge loop was adjusted to a point where the interface would remain at a point 1.5 inches above the top of the packing.

Any change in the manometer readings was adjusted manually with the needle valves through-out the run to provide constant flow rates.

The water and toluene flow rates were measured volumetrically by collecting timed 200 ml. samples of the outlet streams. The change in volume due to the extracted solute was low enough that the exit flow rates could be used as a measure of the inlet flow rates. The amine concentration for all runs was kept below 2.0% by weight.

Samples of the water and toluene product streams were taken at 30 minute intervals and analyzed volumetrically. Sampling was continued until a constant concentration was obtained.

At the completion of a run, the feed streams were turned off and the column was drained before another run was started.

Due to a 7.5-in. section of the column between the interface and the toluene exit point, considerable fluctuation of the amine content

of the toluene stream was experienced. Since the exit concentration of the water stream generally became constant after 4 to 6 hours of operation and its sampling point was only an inch from the packing support, the change in concentration of the water stream was used to determine the amount of solute transferred. On this basis all runs were within $\pm 5\%$ for the material balance between the streams.

METHOD OF CALCULATION OF RESULTS

Theoretical Relations

The results of this investigation have been correlated by the now almost universally accepted method of the "height of a transfer unit," or the H.T.U.

Colburn[3,4] has discussed and shown the advantages of this method. The following are the simplified equations developed by him showing the additivity of the individual film resistances to give the over-all H.T.U. based on a particular phase.

$$(H.T.U.)_{ow} = (H.T.U.)_{w} + (m\ V_w/V_t)(H.T.U.)_{t} \qquad (1)$$

based on the water phase, or

$$(H.T.U.)_{ot} = (H.T.U.)_{t} + (V_t/mV_w)(H.T.U.)_{w} \qquad (2)$$

based on the toluene phase.

The over-all H.T.U. based on the water phase, $(H.T.U.)_{ow}$, or on the toluene phase, $(H.T.U.)_{ot}$, can be calculated from experimental determinations by means of the over-all mass transfer coefficient using the approximate procedure of Elgin and Browning.[6] They showed that if the following assumptions may be made:

1. The distribution of the solute between the two phases is ideal or linear over a concentration range.
2. The moles of each solvent are constant through the extractor.
3. The over-all mass transfer coefficients are constant.

then the rate of mass transfer for extraction based on the water phase may be expressed by the following equation.

$$K_w a = \frac{N/\Theta}{v\,(dC)_{\text{log mean}}} \tag{3}$$

where

$$(dC)_{\text{log mean}} = \frac{(C_{w1} - C^*_{w1}) - (C_{w2} - C^*_{w2})}{\ln \dfrac{(C_{w1} - C^*_{w1})}{(C_{w2} - C^*_{w2})}} \tag{4}$$

The first two assumptions may be approximated if a very low concentration is employed, but the validity of the third assumption is as yet unproved.

Chilton and Colburn[2] relate this transfer coefficient to the height of a transfer unit by the following relationship which is of course subject to the same limitations as the $K_w a$ calculation.

$$(H.T.U.)_{ow} = V_w / K_w a \tag{5}$$

Examination of equation (1) indicates that if the $(H.T.U.)_{ow}$, which can be calculated from experimental data, is plotted as a function of the flow ratio and the distribution constant arranged as mV_w/V_t, a straight line should result with the water film H.T.U. as the ordinate intercept and the toluene film H.T.U. as the slope. These same values may be found as the slope and intercept respectively of a plot of $(H.T.U.)_{ot}$ as a function of V_t/mV_w.

In this work, both of the over-all H.T.U. values were calculated and graphically examined.

The over-all H.T.U. values, $(H.T.U.)_{ow}$ and $(H.T.U.)_{ot}$ are calculated from the same experimental data. The difference lies in the determination of the log mean driving potential, $(dC)_{log\ mean}$. Thus for the water phase values, the operating concentration values are greater than the equilibrium values since the direction of solute transfer is from the water phase. In the toluene phase, the reverse is true. The difference in these values plus some minor effect of the velocity of the two phases is the reason $(H.T.U.)_{ow}$ is not the same as $(H.T.U.)_{ot}$.

In the abcissa term of this method of correlation the distribution coefficient, m, appears. In the ideal situation, m is a constant. However there is generally a small amount of curvature to an actual equilibrium curve so the distribution values at each end of the column are determined and averaged.

The various quantities calculated by the methods discussed are shown in Tables 6, 7 and 8. A sample calculation is shown in the next section.

Sample Calculation

Example, Run I-5

Equipment parameters and experimental values

Superficial area of the column =	0.01228 sq.ft.
Height of the packed section =	4.5 ft.
Superficial velocity of the water phase =	5.90 cu.ft./hr.-sq.ft.
Superficial velocity of the toluene phase =	4.28 cu.ft./hr.-sq.ft.

Analysis of streams	ml of HCl/ml. of sample
Water phase in	5.620
Water phase out	5.400
Toluene phase in	0.000
Normality of the acid used	0.06748 N.

1. Amine content of the water feed.

$$C_{w1} = (5.620 \text{ ml.} \times 0.06748 \text{ N.}) \text{ gm.mol./l.} \times \frac{28.32 \text{ l./cu.ft.}}{453.6 \text{ gm./lb.}}$$

$$= 0.0236 \text{ lb.mol./cu.ft.}$$

2. Amine content of the water product.

$$C_{w2} = (5.400 \text{ ml.} \times 0.06748 \text{ N.}) \text{ gm.mol./l.} \times \frac{28.32 \text{ l./cu.ft.}}{453.6 \text{ gm./lb.}}$$

$$= 0.0228 \text{ lb.mol./cu.ft.}$$

3. Amine content of the toluene product.

$$C_{t2} = (0.0236 - 0.0228) \frac{5.90 \text{ cu.ft./hr.-sq.ft.}}{4.28 \text{ cu.ft./hr.-sq.ft.}} \times \frac{453.6}{28.32}$$

$$= 0.01763 \text{ gm.mol./l.}$$

4. Concentration of a water phase in equilibrium with the toluene phase, C_{t1}.

From Figure 1, when $C_t = 0.01763$ gm.mol./l.

$C^*_{w1} = 0.303$ gm.mol./l. x 28.32/453.6

$= 0.0189$ lb.mol./cu.ft.

5. Molal rate of solute transfer.

$N/\theta = (0.02360 - 0.02280)$lb.mol./cu.ft. x 5.90 cu.ft./hr.-sq.ft. x 0.01228 sq.ft.

$= 0.000058$ lb.mol./hr.

6. Log mean driving force.

$$(dC)_{\text{log mean}} = \frac{(C_{w2} - C^*_{w2}) - (C_{w1} - C^*_{w2})}{\ln \dfrac{(C_{w2} - C^*_{w2})}{(C_{w1} - C_{w1})}}$$

$$= \frac{(0.0228 - 0.000) - (0.0236 - 0.0189)}{\ln \dfrac{(0.0228 - 0.0000)}{(0.0236 - 0.0189)}}$$

$$= 0.01145$$

7. Mass transfer coefficient, $K_w a$.

$$K_w a = \frac{N/\theta}{v \times (dC)_{\text{log mean}}}$$

$$= \frac{0.000058 \text{ lb.mol./hr.}}{0.0541 \text{ cu.ft.} \times 0.01145}$$

$$= 0.0935 \text{ lb.mol./hr.-cu.ft.-unit (dC)}$$

8. Over-all height of a transfer unit.

$$(H.T.U.)_{ow} = V_w/K_w a$$

$$= \frac{5.90 \text{ cu.ft./hr.-sq.ft.}}{0.0935 \text{ lb.mol./hr.-cu.ft.-unit (dC)}}$$

$$= 63.1 \text{ ft.}$$

9. The extraction factor, mV_w/V_t.

C_{w1}	C^*_{t1}	m
0.02360	0.00140	16.89
0.02280	0.00131	17.40
	Average	17.14

mV_w/V_t = 17.14 x 5.90 cu.ft./hr.-sq.ft./4.28 cu.ft./hr.-sq.ft.

= 23.6

Table 6

Experimental and Calculated Quantities for Ethylamine-Toluene-Water

Run No.	Flow Rates		Concentrations		$(dC_w)_{l.m.}$	$K_w a$	$(H.T.U.)_{ow}$
	toluene	water	Water In	Water Out			
I-1	4.28	2.0	0.02398	0.02220	0.0150	0.0537	37.2
I-2	4.28	3.74	0.02398	0.02300	0.01638	0.0507	73.7
I-3	4.28	10.4	0.02579	0.02522	0.0956	0.0141	75.0
I-4	4.28	6.13	0.02579	0.02490	0.0155	0.0798	76.8
I-5	4.28	5.90	0.02360	0.02280	0.01145	0.0935	63.1
I-6	5.20	2.77	0.02360	0.02239	0.01692	0.0448	61.8
I-7	4.28	3.26	0.02240	0.02090	0.0131	0.0846	38.5

Run No.	m_1	m_2	m_{avg}	mV_w/V_t	V_t/mV_w	$(dC_t)_{l.m.}$	$K_t a$	$(H.T.U.)_{ot}$
I-1	15.32	16.91	16.11	7.54	0.133	0.00109	0.737	5.81
I-2	17.03	16.98	17.00	14.8	0.0674	0.000339	2.45	2.45
I-3	16.8	16.8	16.8	40.7	0.0245	0.000581	2.31	1.85
I-4	16.8	16.95	16.93	24.3	0.0412	0.000700	1.77	2.42
I-5	16.89	17.40	17.14	23.6	0.0424	0.000686	1.56	2.74
I-6	17.91	16.89	17.44	9.29	0.1076	0.000357	2.13	2.44
I-7	17.05	17.15	17.10	13.0	0.0768	0.000533	2.08	2.06

Table 7

Experimental and Calculated Quantities for Diethylamine-Toluene-Water

Run No.	Flow Rates		Concentrations		$(dC_w)_{l.m.}$	$K_w a$	$(H.T.U.)_{ow}$
	toluene	water	water in	water out			
II-1	5.20	5.00	0.00802	0.00489	0.00408	1.275	3.92
II-2	5.20	2.70	0.00802	0.00310	0.00347	1.275	2.02
II-3	5.20	3.20	0.00802	0.00336	0.00351	0.962	3.33
II-4	4.28	8.40	0.01175	0.00863	0.00602	0.985	8.53
II-5	4.28	6.00	0.01175	0.00791	0.00611	0.850	7.06
II-6	4.28	10.1	0.01232	0.00952	0.00654	0.978	10.3
II-7	4.28	7.13	0.01232	0.00820	0.00599	1.110	6.42

Run No.	m_1	m_2	m_{avg}	mV_w/V_t	V_t/mV_w	$(dC_t)_{l.m.}$	$K_t a$	$(H.T.U.)_{ot}$
II-1	1.22	1.54	1.38	1.33	0.754	0.00221	2.36	2.20
II-2	1.22	1.61	1.41	0.732	1.36	0.00285	1.55	3.36
II-3	1.23	1.61	1.42	0.953	1.15	0.00279	1.21	4.30
II-4	1.49	1.50	1.50	2.94	0.341	0.00346	1.66	2.58
II-5	1.49	1.51	1.50	2.10	0.476	0.00372	1.40	3.06
II-6	1.50	1.50	1.50	3.54	0.272	0.00348	1.84	2.33
II-7	1.58	1.46	1.52	2.53	0.395	0.00262	2.54	1.69

Table 8

Experimental and Calculated Quantities for Triethylamine-Toluene-Water

Run No.	Flow Rates		Concentrations		$(dC_w)_{l.m.}$	$K_w a$	$(H.T.U.)_{ow}$
	toluene	water	water in	water out			
III-1	4.28	3.20	0.01342	0.00024	0.00308	3.1	1.03
III-2	4.28	6.02	0.01369	0.00169	0.00532	3.07	1.96
III-3	4.28	10.4	0.01210	0.00219	0.00493	4.74	2.20
III-4	2.54	5.20	0.01210	0.00072	0.00351	3.82	1.36
III-5	5.82	3.20	0.01295	0.00089	0.00434	2.02	1.59
III-6	1.51	4.50	0.01295	0.00144	0.00436	2.68	1.68
III-7	1.35	4.00	0.01185	0.00078	0.00331	3.03	1.32

Run No.	m_1	m_2	m_{avg}	mV_w/V_t	V_t/mV_w	$(dC_t)_{l.m.}$	$K_t a$	$(H.T.U.)_{ot}$
III-1	.0802	.1652	.1227	0.0915	10.9	0.0653	0.146	29.3
III-2	.0822	.1000	.0911	0.1282	7.8	0.1015	0.161	26.6
III-3	.0841	.0920	.0880	0.214	4.78	0.0599	0.391	10.95
III-4	.0841	.1090	.0965	0.198	5.06	0.0394	0.340	7.49
III-5	.0828	.2030	.1429	0.0784	12.75	0.0256	0.341	17.1
III-6	.0834	.1092	.0963	0.298	3.48	0.0395	0.297	5.08
III-7	.0846	.1083	.0964	0.286	3.51	0.0370	0.271	4.98

RESULTS

The experimental data of this investigation has been correlated by the H.T.U. method. (See preceding chapter.)

Figure 7 shows the variation of the over-all H.T.U. based on the water phase with the variation of the extraction factor (mV_w/V_t), and Figure 8 shows the variation of the H.T.U. based on the toluene phase with the inverse extraction factor.

The difficulty of constructing a representative line through the experimental points is obvious from the spread of the points indicated. According to equation (1) and (2), the intercept of Figure 8 should equal the slope of Figure 7, and the slope of Figure 8 should equal the intercept of Figure 7. Since the distribution coefficient, m, for ethylamine is large, averaging about 17, examination of equation (1) indicates that the $(H.T.U.)_w$ may be very small or that the $(H.T.U.)_t$ may be the controlling resistance if the film values are assumed to be of the same relative magnitude. This would indicate a zero intercept for Figure 7 and a zero slope for Figure 8. The line shown in Figure 7 is a root mean square line with the liability of error limited to the derived ordinate variable. A similar type line is shown for Figure 8. The individual film values obtained from these two figures may be compared in this fashion.

	Figure 7	Figure 8
$(H.T.U.)_t$	slope = 3.75	intercept = 2.32 feet

Figures 9 and 10 show similar data for the diethylamine-toluene-water system. Clearly the intercept of Figure 9 should be zero, thus

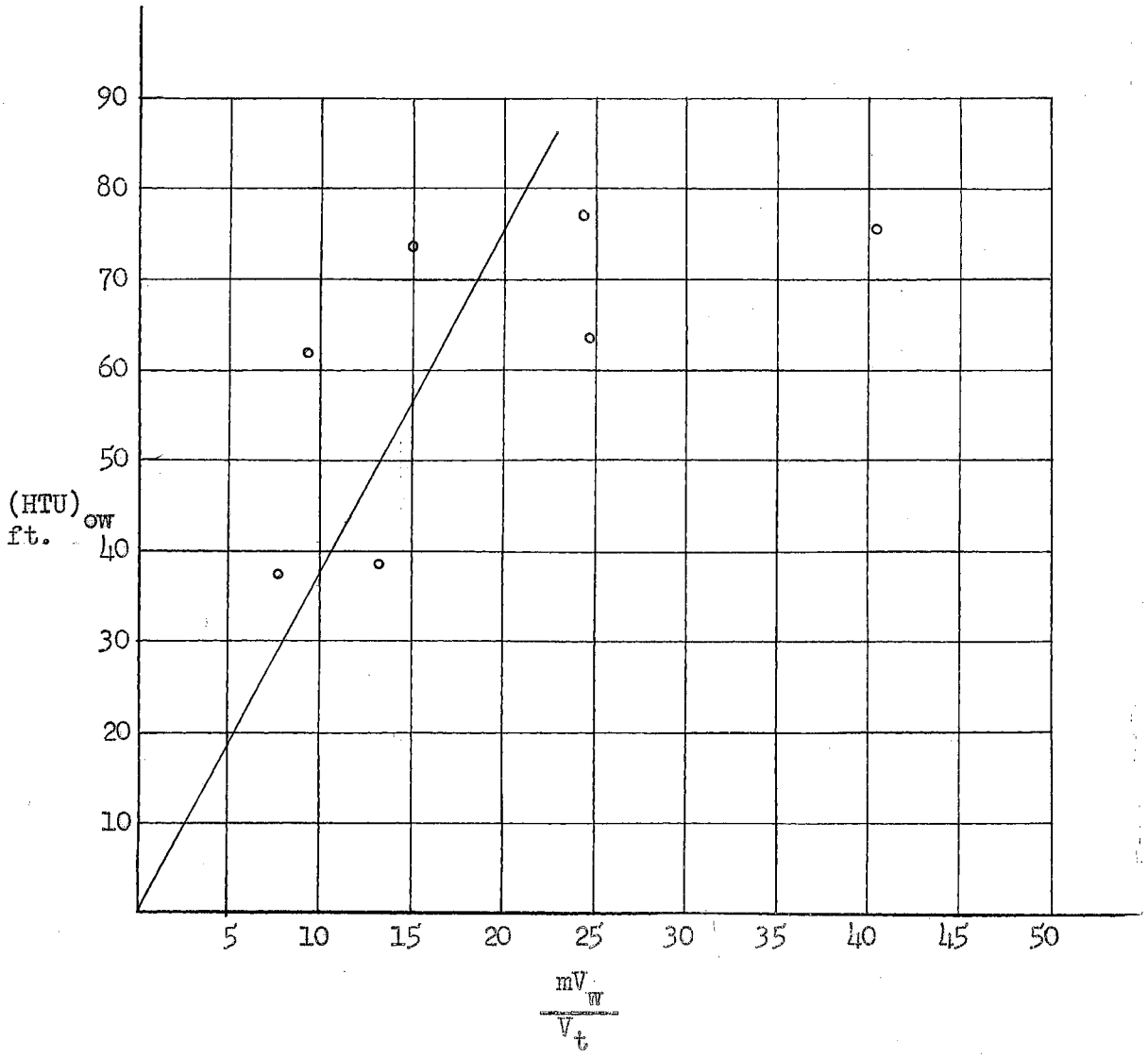


Figure 7

Experimental Runs $(H.T.U.)_{ow}$ Against $m\frac{V_w}{V_t}$ Ethylamine-Toluene-Water

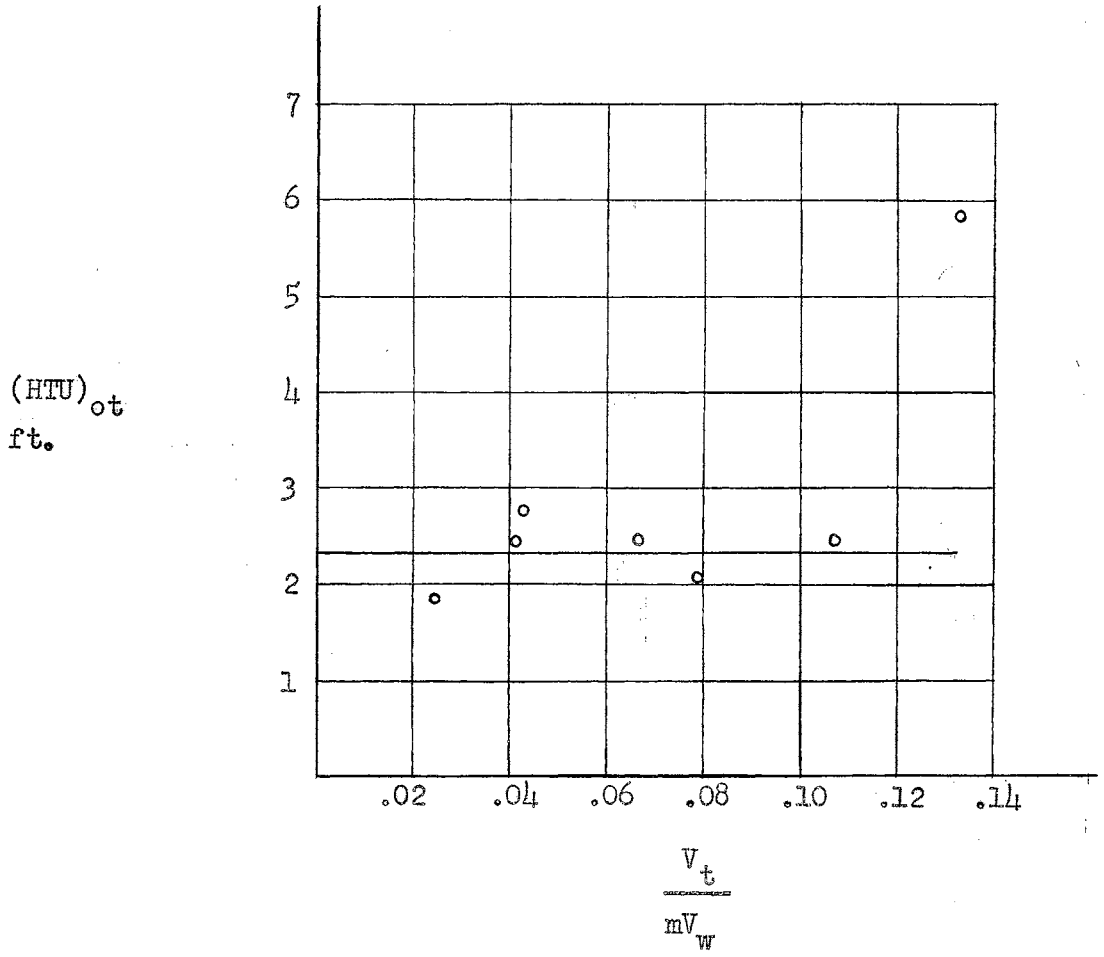


Figure 8

Experimental Runs $(HTU)_{ot}$ Against $\frac{V_t}{mV_w}$

Ethylamine-Toluene-Water

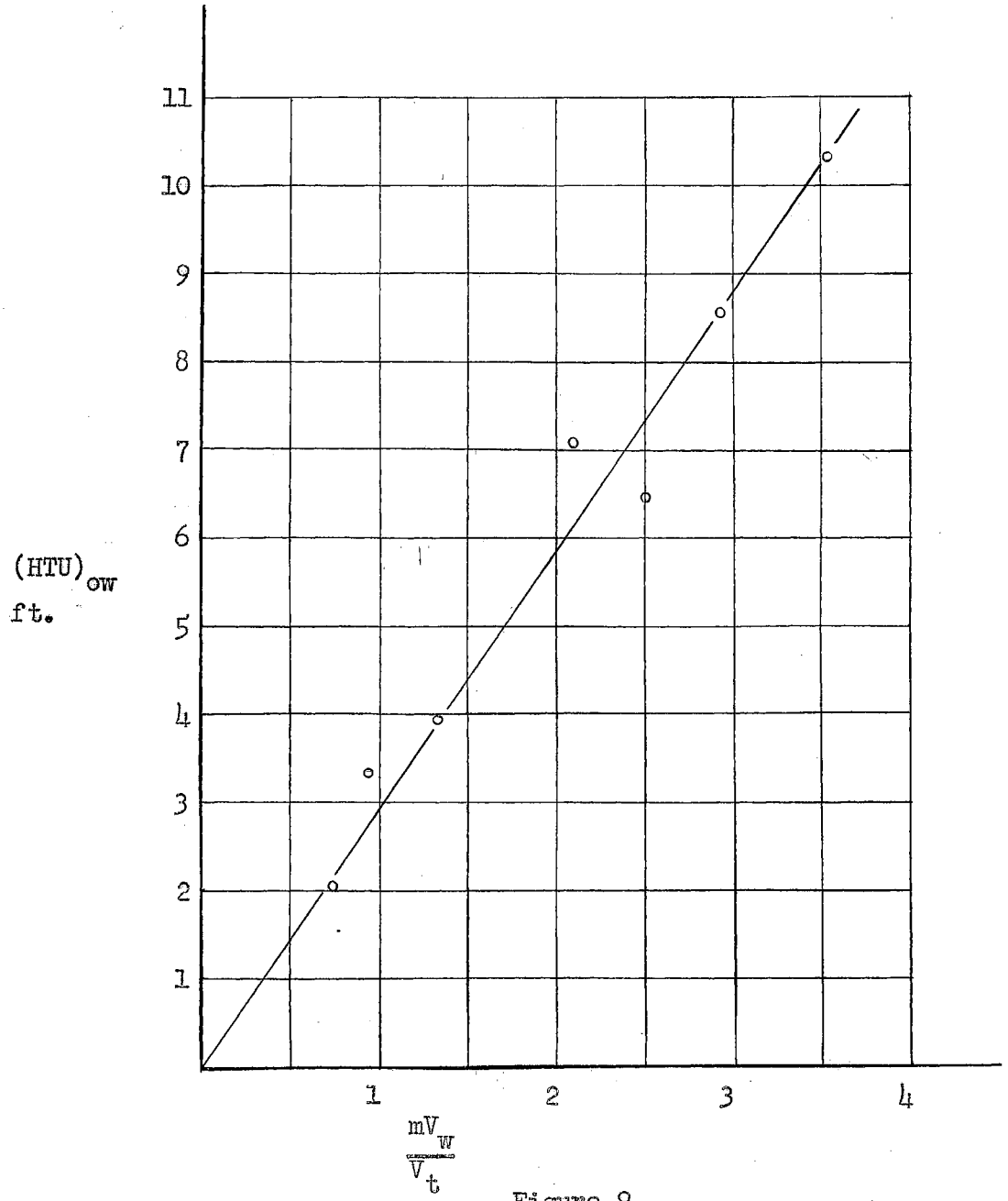


Figure 9

Experimental Runs $(HTU)_{ow}$ Against $m\frac{V_w}{V_t}$

Diethylamine-Toluene-Water

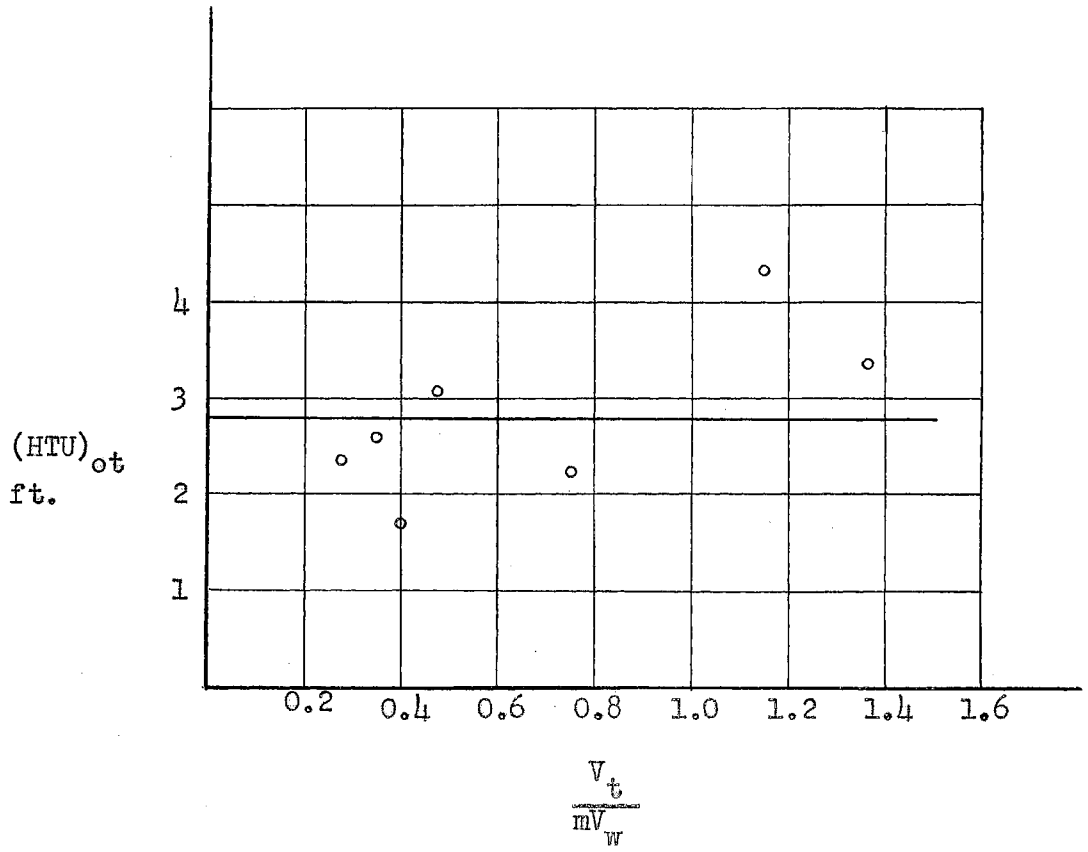


Figure 10

Experimental Runs $(HTU)_{ot}$ Against $\frac{V_t}{mV_w}$

Diethylamine-Toluene-Water

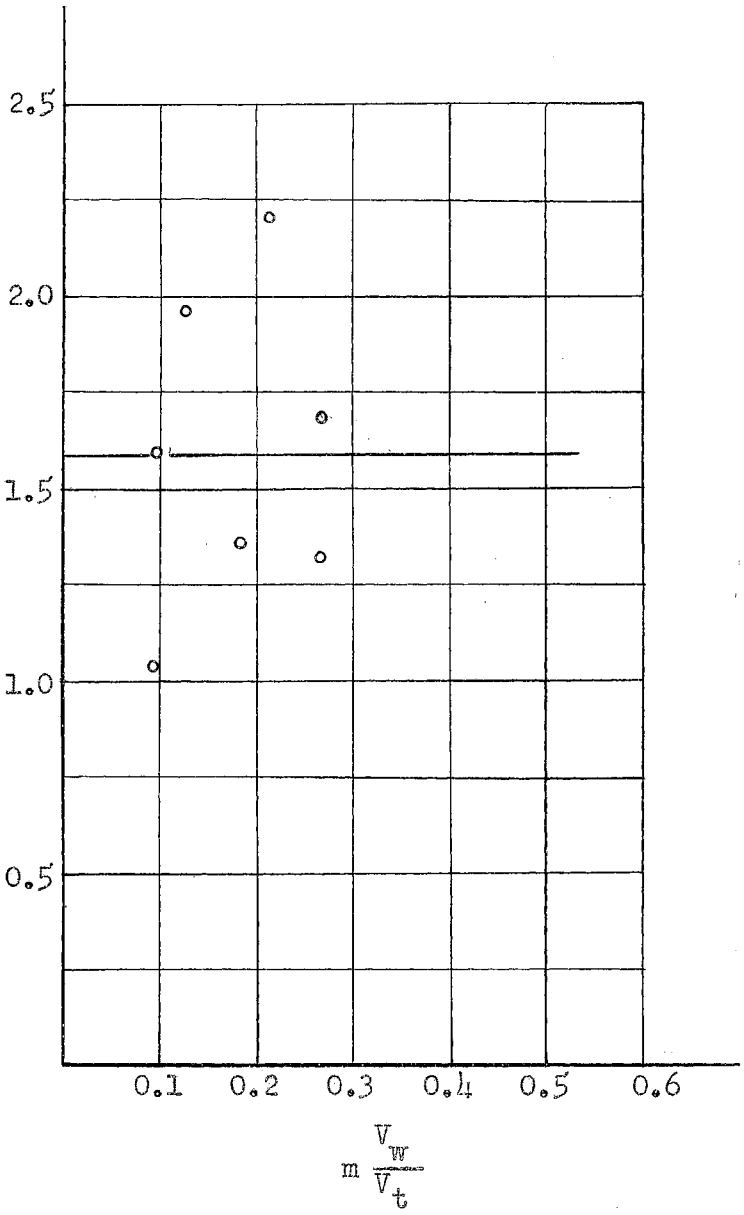


Figure 11

Experimental Runs $(HTU)_{ow}$ Against $m\frac{V_t}{V_w}$

Triethylamine-Toluene-Water

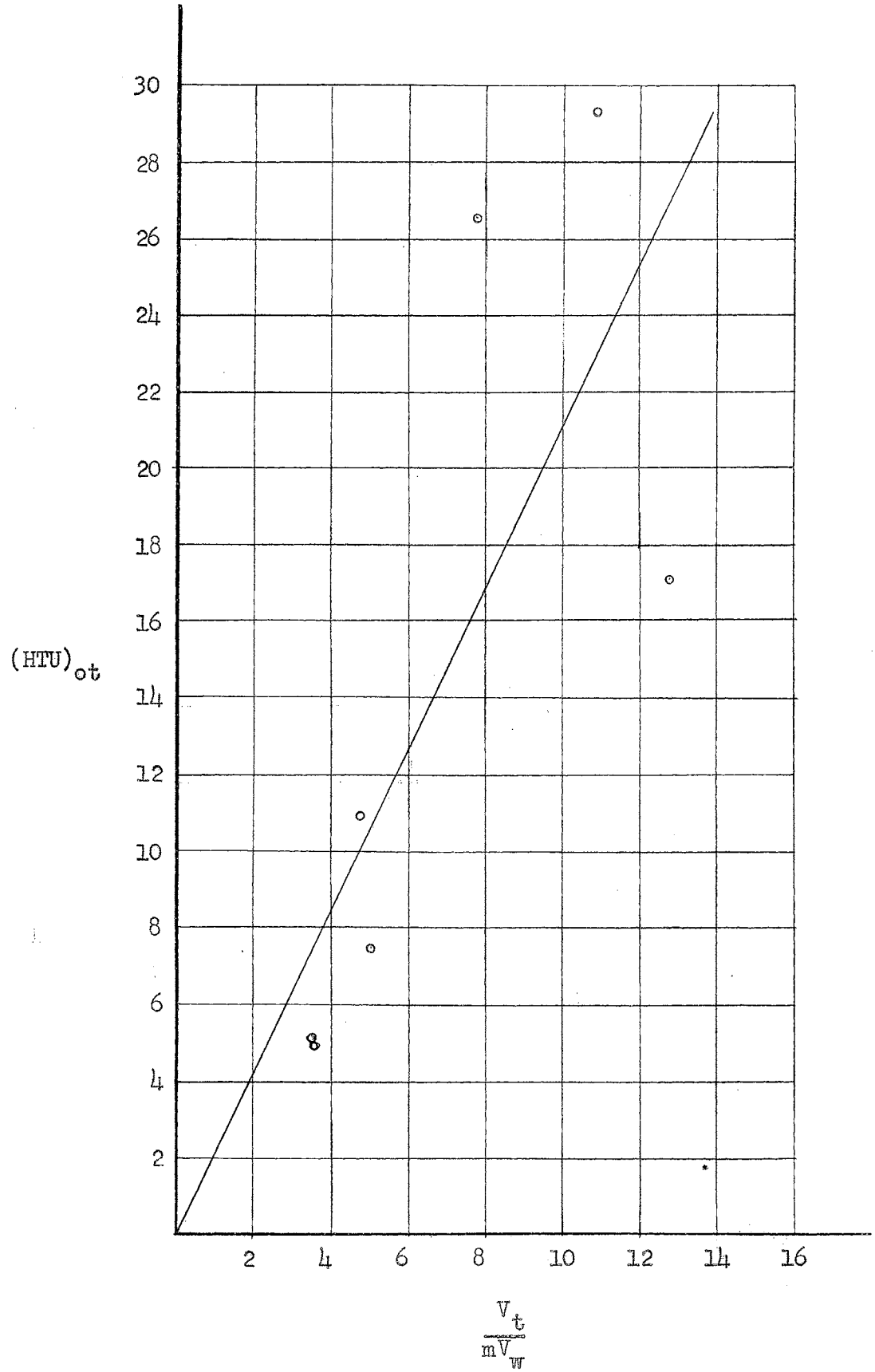


Figure 12

Experimental Runs $(HTU)_{ot}$ Against $\frac{V_t}{mV_w}$

Triethylamine-Toluene-Water

indicating a negligible resistance in the water film. This helps verify the choice of the zero intercept used in Figure 7 since a zero water film resistance is noted with a distribution value averaging about 1.5. It would seem logical to choose zero for the value when the distribution coefficient is as large as 17.

The data obtained for the triethylamine-toluene-water system is presented in Figures 11 and 12. For this sytem, the principal resistance is in the water phase as might be suspected from its low distribution coefficient which averages about 0.1. Equation (1) indicates that the principal resistance should be in the water phase when the distribution coefficient is very low. The representative lines used for Figures 11 and 12 can only be reconciled by careful consideration of the experimental data and of the theoretical considerations. It would be quite plausible to draw the lines in both figures from the origin. However once this is done for one graph, the theory indicates that the corresponding function based on the other phase must have a zero slope. Thus the zero slope seems to fit Figure 11 more closely.

The slopes and intercepts obtained from Figures 7-12 are summarized in Table 9.

The height of the individual transfer units obtained from the slope of Figures 7, 9 and 12 are shown in Figure 13 as a function of the diffusivity of the solute in the controlling film. Thus Figures 7 and 9 produce $(H.T.U.)_t$ film values which are plotted against the diffusivity of the solute in the toluene film, while Figure 12 produces an $(H.T.U.)_w$ film value which is plotted against the solute diffusivity in the water film. These same H.T.U. film values are shown in Figure 15 as a function of the molecular weight of the diffusing solute, and in Figure 14 as a function of the molal volume of the solute.

Table 9

Individual Film H.T.U. Values

	$(H.T.U.)_t$	$(H.T.U.)_w$
Ethylamine		
Figure 7	3.75	0.00
Figure 8	2.32	0.00
Diethylamine		
Figure 9	2.94	0.00
Figure 10	2.79	0.00
Triethylamine		
Figure 11	0.00	1.59
Figure 12	0.00	2.10

DISCUSSION OF RESULTS

Over-all H.T.U. Values

The results of series I and III, for ethylamine and triethylamine diffusing, were somewhat disappointing with regard to the deviation of the results. The most reasonable approach to the reason for the large deviation seems to be from an approach to equilibrium standpoint. The mean driving potential which is used to determine the coefficient of transfer involves the difference between the outlet concentration of a stream and the concentration of a stream which would be in equilibrium with the other phase entering at that point. As this difference becomes very small, or as equilibrium conditions are approached, the determination of the mean driving potential becomes less precise. The exit solution strength of the toluene phase was found in some instances to be near the equilibrium value and the experimental error of measurement may be greater than the difference between the operating and equilibrium values. This would affect the $K_w a$ calculation and hence the H.T.U. values.

Figures 8 and 10, the ethylamine and diethylamine extractions based on the toluene phase show reasonably close adherence to the derived line except at the higher (V_t/mV_w) values. Such effects have been noted in previous work[10] and have been attributed to a possible coalescing of the dispersed toluene phase at high values of toluene flow. Such coalescing, or channeling of the dispersed phase will lower the interfacial area and thereby increase the difficulty of separation. This will appear

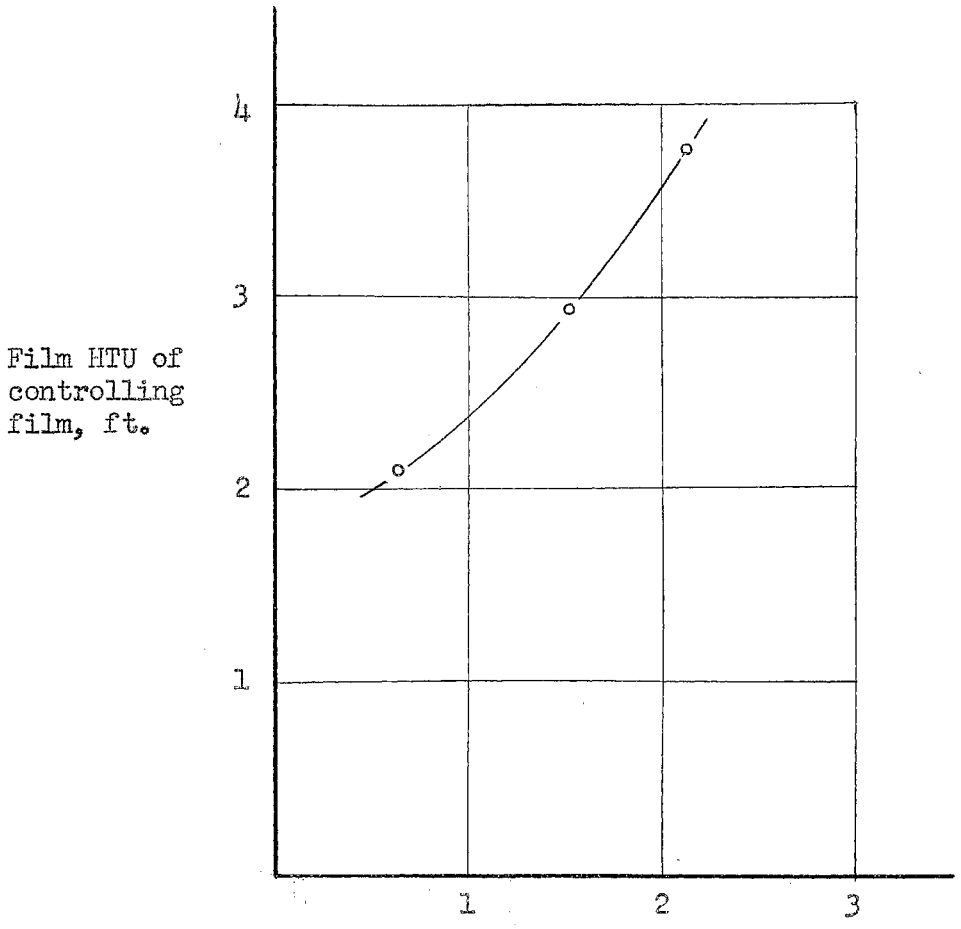


Figure 13

Effect of Diffusivity of Solute

on the Individual Film H.T.U.

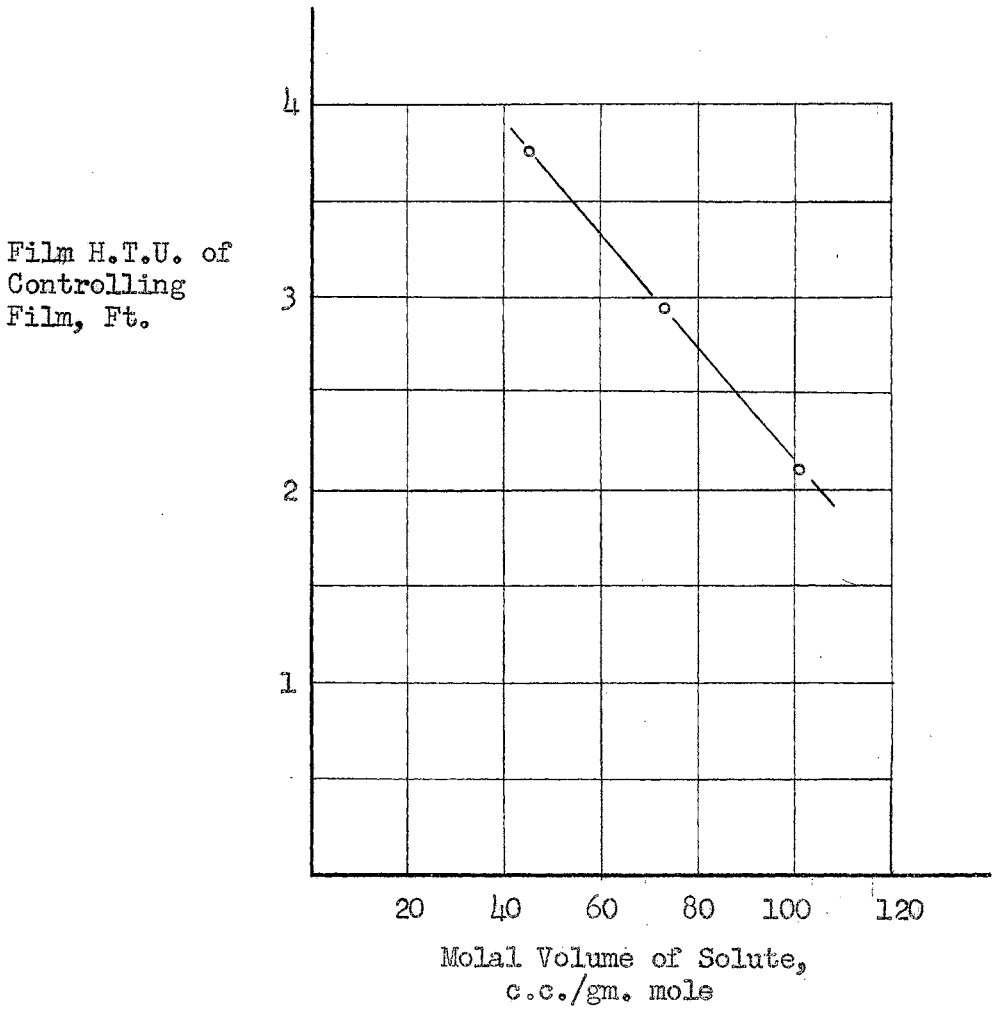


Figure 14

Effect of the Molal Volume of the Solute on the Individual Film H.T.U.

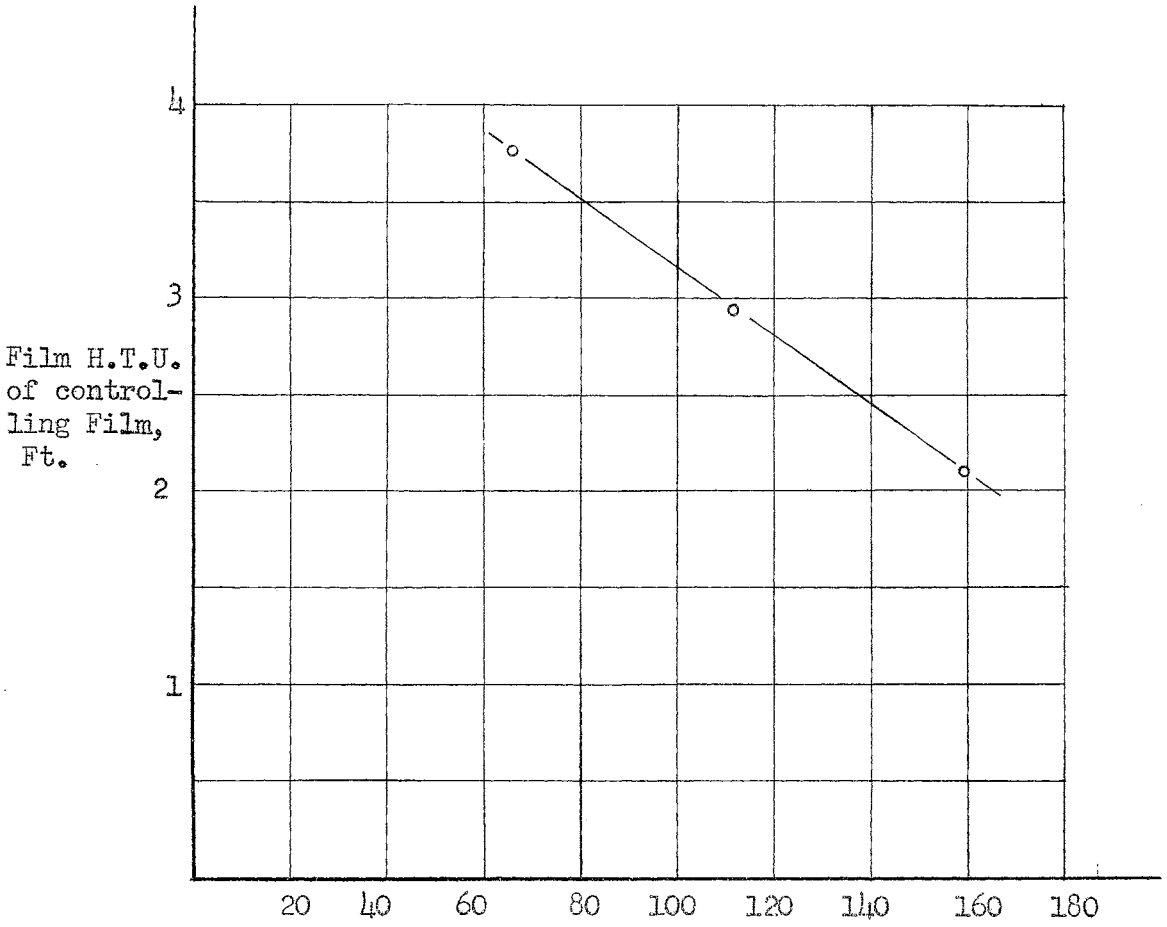


Figure 15

Effect of the Molecular Weight of the

Solute on the Individual Film H.T.U.

as increased heights of the transfer units. This effect is noted for the ethylamine and diethylamine extractions.

Film H.T.U. Values

The individual film H.T.U. values, determined from the slope of Figures 7, 9 and 12 are shown as functions of physical properties of the diffusing solutes in Figures 13, 14 and 15.

The variation of the film values with the molal volume of the solute, Figure 14, and with the molecular weight, Figure 15, may not be significantly independent but both relationships are shown.

For the three amines under consideration, the molecular weight serves to give some indication of the structural similarity of the solute to the two phases. It appears from the results obtained here that the principal diffusional resistance occurs in the phase which is less congruous to the solute in question.

The molal volume of the diffusing solute is a measure of the molecular size of the solute. The relationship in Figure 14 shows that the H.T.U. of the controlling film decreases with increasing molecular size. This may possibly be interpreted as meaning the difficulty of separation is greater for a larger molecule.

Figure 13 shows increasing H.T.U. values corresponding to increased values of the diffusion coefficient. This is interpreted to indicate the difficulty of effecting a given separation is less for substances which have higher diffusivities, or that faster moving molecules have less film resistance to extraction than do slower moving ones.

NOMENCLATURE

a = interfacial area of contact per cu. ft. of tower, sq.ft./cu.ft.

C = solute concentration in main stream, lb.moles/cu.ft.

C^* = solute concentration in one phase which would be in equilibrium with observed concentration in other phase, lb.moles/cu.ft.

$(dC)_{l.m.}$ = log mean concentration difference, lb.moles/cu.ft.

D = diffusion coefficient, sq.cm./sec.

(H.T.U.) = height of a transfer unit, ft.

$(H.T.U.)_o$ = over-all height of a transfer unit, ft.

Ka = over-all mass transfer coefficient, lb.moles/(hr.)(cu.ft.)(lb.moles/cu.ft.)

m = distribution coefficient, ratio of solute concentration in aqueous phase to that in nonaqueous phase at equilibrium.

N = number of lb.moles of solute transferred

V = liquid flow rate, cu.ft./(hr.)(sq.ft. of tower cross-section)

v = effective volume of column, cu.ft.

θ = time, hr.

Subscripts

w = water phase

t = toluene phase

$1, 2$ = ends of the tower

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